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Characterization and chlorine reactivity of particulate matter released by bathers in indoor swimming pools

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Abbreviations: BCAA (Bromochloroacetic acid); BCAN (Bromochloroacetonitrile); BDCAA (Bromodichloroacetic acid); BDCM (Bromodichloromethane); BFA (Body fluid Analogs); BV (Bed volume); CH (Chloral hydrate); DBAN (Dibromoacetonitrile); DBCM (Dibromochloromethane); DOM (Dissolved organic matter); DBPs (Disinfection by-products); DCAA (Dichloroacetic acid); DCAN (Dichloroacetonitrile); DOC (Dissolved organic carbon); FBW (Filter backwash (waste)water); GC-ECD (Gas chromatography electron capture detector); HAAs (Haloacetic acids); HANs (Haloacetonitriles); KN (Kjeldahl nitrogen); LLE (Liquid-liquid extraction); MCAA (monochloroacetic acid); MTBE (Methyl-tertio-butyl-ether); NPOC (Non-purgeable organic carbon); NTU (Nephelometric turbidity unit); POM (Particulate organic matter); TBM (Tribromomethane or bromoform); TCAA (Trichloroacetic acid); TCM (Trichloromethane or chloroform); TCP (1,1,1-trichloropropanone); THMs (Trihalomethanes); TOC (Total organic carbon).

Abstract

Disinfecting swimming pool water is essential for preventing waterborne diseases. An unforeseen consequence of treating water with disinfectants is the formation of disinfection by-products (DPBs) that can cause harmful effects to health through the interactions between the added disinfectant and organic matter in the water. The present work focuses on the chlorine reactivity with particles released by bathers. Such particles are collected in the filter backwash water of swimming pools and this study intends to distinguish DPBs generated from dissolved chemicals from those formed by particulate matter. Therefore, filtered and unfiltered backwash waters were collected from several swimming pools, analyzed physicochemically and chemically, and then chlorinated as is (79 mgL⁻¹) and as diluted suspensions (36.2 and 11.9 mgL⁻¹) at varying concentrations of chlorine (1.2 mg and 24 mgCl₂L⁻¹). Utilizing a DPD colorimetric technique and GC-ECD, respectively, the kinetics of chlorine consumption and DPBs production have been investigated. Up to 25.7 µgL⁻¹ of chloroform was produced within 96 h at 1.2 mgCl₂L⁻¹, followed by haloacetic acids (HAAs) and haloacetonitriles (HANs). Within 96 h, the concentration of trichloroacetic acid reached a maximum of 231.8 µgL⁻¹ at a chlorine concentration of 231.8 µgL⁻¹. The formations of 0.13 µmol THMs, 0.31 µmol HAAs, and 0.04 µmol HANs per mg of dissolved organic carbon (DOC) were finally determined by correlating the organic content of particles with the nature of the DBPs generated. Comparing the quantities of DBPs generated in filtered and unfiltered samples helps us conclude that ~50%

of DBPs formed during the chlorination of swimming pool water are derived from particles brought by bathers.

Keywords: disinfection byproducts; chlorination; particles; filter backwash wastewater; pollutant release

1. Introduction

Disinfecting swimming pool water is necessary to prevent the outbreak of diseases caused by bather-borne pathogenic microorganisms (WHO, 2006). Chlorine or chlorine-based compounds are the most popular chemical disinfectants owing to their efficacy and low overall relative cost. However, using chlorine-based disinfectants affords the formation of undesirable disinfection by-products (DBPs), which are formed by the reaction of organic and inorganic compounds brought by bathers (Manasfi et al., 2017a), such as mineral salts or organic compounds including urea (from urine and sweat), creatinine (from sweat), and amino acids (Lian et al., 2014). Further, more than 100 DBPs, including trihalomethanes (THMs), haloacetamides, haloketones, haloacetic acids (HAAs), haloacetaldehydes, halonitromethanes, haloacetonitriles (HANs), halogenated cyanogens, halophenols, halobenzoquinones, and *N*-nitrosamines have been identified in swimming pool water (Richardson et al., 2010; Xia et al., 2012; Weng et al., 2013; Daiber et al., 2016; Li and Blatchley, 2017; Manasfi et al., 2017a). The majority of them are known to have adverse health effects for indoor swimming pool users (swimmers and workers as lifeguards) (Westerlund et al., 2019; Couto et al., 2021; Han et al., 2021; Manasfi et al., 2017b), as being cytotoxic, genotoxic, and mutagenic *in vitro* or *in vivo* (Deng et al., 2014; Wagner and Plewa, 2017; Liberatore et al., 2022; Wu et al., 2022). For instance, trichloramine (NCl_3) causes the most irritating symptoms (Fantuzzi et al., 2010; Villanueva et al. 2015), whereas THMs may cause adverse effects on the reproductive system, liver, kidneys, and nervous system as well as potential long-term risks for the development of cancers (Bessonneau et al., 2011; Zazouli and Kalankesh. 2017).

Swimming pool users are exposed to DBPs via three routes: Inhalation (e.g. NCl_3 , THMs, and cyanogen chloride), dermal absorption (e.g. chloroform, haloketones, chloral hydrate, and halophenols), and/or ingestion (Li and Blatchley. 2007; Trabaris et al., 2012).

In addition to the type and the management of the water (and air) treatment chain in swimming pools, the hygienic behavior of bathers can considerably minimize the inputs of DPB precursors in the pool (Keuten et al., 2012; 2014; Skibinski et al., 2019). Combining sand filtration with granular activated carbon filtration has been proven to be the most effective treatment for reducing DBPs and their precursors; however, conventional water treatment techniques combining (or not combining) coagulation and sand filtration remain the most widely utilized methods (Lee et Blatchley, 2022). Nonetheless, during the filtration step, dissolved and undissolved compounds are retained on the filter media (Amburgey et al., 2012), where they are exposed to chlorinated water and can form new or additional DBPs, until the backwashing process is initiated (Skibinski et al., 2016). The reactivity between chlorine and DOM brought by bathers has been the subject of numerous studies, and a solution simulating DOM brought by bathers has been formulated (body fluid analogs (BFA)) (Borgmann-Strahsen., 2003; Goeres et al., 2004; Judd and Black., 2000; Judd and Bullock., 2003). Till date, the reactivity of chlorine with particulate organic matter (POM) has been poorly documented. Nonetheless, this fraction of pollutants transported by bathers is an important source of DBP precursors as highlighted by the two available studies on this topic. Accordingly, Kim et al. (2002) showed that the addition

of anthropogenic particles to pool water increased the concentration of total organic carbon (TOC). In addition, DBP concentrations in chlorinated swimming pool water increased when more organic particles were added. Moreover, Hansen et al. (2012) estimated that the DPB production potential from particles was $\sim 4 \mu\text{molmgDOC}^{-1}$ for THMs, $9.6 \mu\text{molmgDOC}^{-1}$ for HAAs, and $1.6 \mu\text{mol mgDOC}^{-1}$ for HANs. Furthermore, they were more than the DBP production potential discovered by Kanan and Karanfil (2011) from the chlorination of BFA or DOM: 0.62 and $0.26 \mu\text{molmgDOC}^{-1}$ for THMs and HAAs, respectively (HANS not determined).

POM is mostly composed of hair containing amino acids (cysteine, serine, and glutamic acid), skin flakes containing lipids, and components issued from personal care products such as sunscreen lotions containing titanium dioxide or zinc oxide to inhibit UV radiation from reaching the skin (ANSES, 2020; Jeon et al.; 2016). In this regard, microorganisms are sometimes considered as particles (Keuten et al., 2012, Zwiener et al., 2007), including viruses ($0.02\text{-}0.3 \mu\text{m}$), bacteria ($0.5\text{-}5 \mu\text{m}$), or protozoa ($5\text{-}50 \mu\text{m}$), in addition to their resistance forms such as spores, cysts, or oocysts (ANSES, 2020). According to Keuten et al. (2012; 2014), the average total particle release of bathers (organic and inorganic) for a 30-minute activity amounts to 14.6×10^9 particles ($2\text{-}50 \mu\text{m}$) per bather; however, there are considerable differences based on the individual characteristics of the bathers (between 9.7×10^5 and 6.3×10^7 particles in the first 30 seconds of immersion).

The current study attempts to contribute to a greater understanding of the physical and chemical features of particles released by bathers and their interaction with chlorine. To achieve this, between 2020 and 2022, five sampling campaigns were conducted in two swimming pools to collect water and particles directly at the discharge site of filter backwash water (FBW). Correspondingly, onsite measurements of various physicochemical parameters (free and total chlorine, pH, turbidity, and conductivity) were followed by laboratory characterization of particles using granulometry (particle-size distribution), microscopic observations, and in terms of carbon and nitrogen contents. At constant pH and at various initial free chlorine concentrations, the examined particles were further chlorinated as such or as diluted suspensions, followed by spectrophotometry and by GC-ECD, respectively, to monitor the consumption of chlorine and the type and concentrations of DBPs produced. In particular, 14 DBPs, including four THMs, three HANs, five HAAs, one haloaldehyde (chloral hydrate, CH), and one haloketone (1,1,1-trichloropropanone, TCP), were analysed. Furthermore, the separate chlorination of particles retained on a $0.7\text{-}\mu\text{m}$ filter and of the resulting filtrate, has allowed DBPs formed by particles to be distinguished from DBPs formed by DOM.

2. Materials and methods

2.1 Description of swimming pools under study

Five sampling campaigns have been conducted in two indoor municipal swimming pools located in Western France between September 2020 and February 2022, namely four campaigns in swimming pool A (PA) and one campaign in swimming pool B (PB), shortly prior to closing. PA had a recreational pool, a competition pool, and a children's pool. Meanwhile, PB had a recreational pool, a competition pool, and a training pool. Each pool type in PA and PB was equipped with its own hydraulic circuit. Following the order of the various campaigns, PA pool attendances were 100, 94, 100, and 276 bathers each day in various pools. The sampling period matching to school breaks accounted for the disparity in the turnout between the fourth campaign and the others. Moreover, in PA, which is located near the Atlantic Ocean, attendance may fluctuate according to the weather conditions; in the summer, bathers may choose to swim in PA or in the Atlantic Ocean. Daily attendance at PB was 170 bathers.

Both swimming pools employed chlorine (Cl_2) as a disinfectant, automatically regulated to 1.4-1.5 $\text{mgCl}_2\text{L}^{-1}$, and sand filters comprised of flint (4400 kg; particle size: 0.4-0.8 mm) and sand (575 kg; 1-2 mm). In contrast to PB filters, PA filters comprised an additional layer of hydroanthracite (1300 kg), and polyaluminium chloride (PAX-XL7; 8L per week) as coagulant was used prior to the filtration process. The volume of the filter media was calculated by adding the estimated volumes of each layer, considering their respective masses in the filter and densities as dried material (1600 kgm^{-3} for flint, 1500 kgm^{-3} for sand, and 850 kgm^{-3} for hydroanthracite). In addition, the bed volumes (BV) were determined by dividing the estimated FBW volume that exited the filter backwash circuit for a single sample by the volume of the filtration material.

Pool water renewal rates of 8 m^3 per day in PA ($56 \text{ L.bather}^{-1}.\text{day}^{-1}$) and 7.7 m^3 per day in PB ($44.5 \text{ L.bather}^{-1}.\text{day}^{-1}$) exceeded the French limits for swimming pool water renewal in swimming pools ($30 \text{ L.bather}^{-1}.\text{day}^{-1}$).

Filters were backwashed either with ultrafiltered water (PA) issued from previous backwashing processes or with water from pools (PB).

In PA and PB, the frequency of filter cleaning (backwashing) was often increased when the water flow rate at the outlet of the filter media dropped below 70% of the original flow rate. To capture the water and particles released by these backwashes, the backwashes were rolled out during sampling periods. The previous backwashing processes were conducted for 5 d (PA1, PA3, and PA4), 15 d (PA2), and 7 d (PB) prior to our sampling sessions. The duration of the backwashing process for both pools was 4.5 min.

Figure 1 summarizes both swimming pool designs and treatment chains.

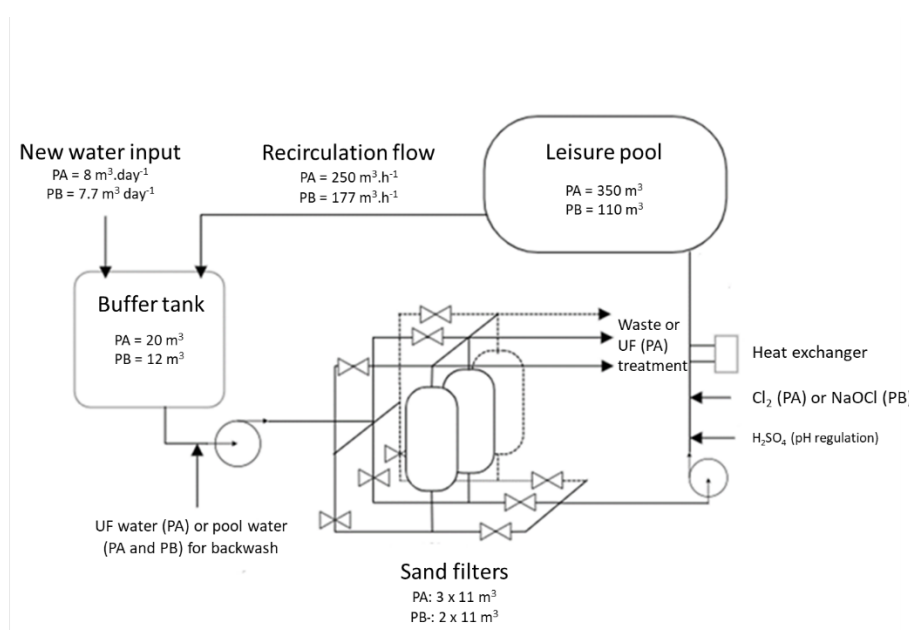


Figure 1. Diagram of the hydraulics at swimming pool A (PA) and swimming pool B (PB) swimming pool (UF = ultrafiltration).

2.2 Description of sampling campaigns

The first campaign in PA (PA1) allowed us to measure turbidity and particle concentration trends across the course of filter washing. During the second campaign (PA2), the swimming pool was only accessible to schools (period of semi-confinement due to COVID-19). This allowed us to determine the carbon and nitrogen releases (in water and in particles) from these

particular users. During the third (PA3) and fourth (PA4) campaigns, the swimming pool was reopened to the public and we were able to recover particles released by bathers (from any age category).

In each sampling campaign, three types of water samples were collected as follows. i) Pool water collected in the technical room of PA (access to the leisure pool was forbidden), and pool water collected in the leisure pool of PB; ii) filling water (from public water works) in both pool technical rooms; and, iii) FBW samples collected by fractions throughout the backwashing process using consecutive and alternative use of 1-L polyethylene bottles without reagent (for onsite measurement of physicochemical parameters) and 5-L polyethylene cans containing sodium thiosulfate (for further analysis of DBPs).

2.3. Analytical methods

2.3.1. Chemicals and reagents

Analytical standards including halogenated volatile mix (containing HANs) and mix HAAs were purchased from Agilent products. Chloral hydrate, THM calibration mix, 2,3-dibromopropionic acid solution, and 1,2-dichloropropane were purchased from Supelco (USA). A standard stock solution of each mixture was produced in Merck-purchased (Germany) methyl *tert*-butyl ether (MTBE, 99.8% purity). L-ascorbic acid, and sodium sulfate anhydrous reagent grade was purchased from Sigma (China). In addition, analytical grade sulfuric acid was bought from Fisher Scientific (UK).

Sodium hypochlorite solution (10% purum) was purchased from Fluka™ (USA) and was diluted before chlorination assays.

Ultrahigh-quality deionised water (resistivity > 18 MΩ.cm; TOC < 50 µgC.L⁻¹) was obtained using a Millipore MilliQ Plus TOC system (Bedford, MA, USA).

2.3.2. Sample analysis

On site analyses

pH and conductivity were measured using a multimeter (WTW Multi 3430, Xylem, USA) and two electrodes (Suntix 940[®] for pH and TetraCon 925[®] for conductivity). In addition, the free and total chlorine were determined via the DPD colorimetric method using a 10 mL sample and a Merck Spectroquant-NOVA 60 (Darmstadt, Germany) at 525 nm with a VWR DPD free chlorine test (West Chester, Pennsylvania, USA). The total chlorine was subtracted from free chlorine to calculate the combined chlorine (+/- 0.1 mgCl₂.L⁻¹). Additionally, the turbidity was measured via a turbidimeter (Ponsel Acteon 5000 + SN-PNEPB sensor, Aqualabo, France) directly in the 1L-polyethylene bottles used to collect the samples.

2.4.2 Laboratory analyses

TOC and dissolved organic carbon (DOC) were determined with a TOC-meter (TOC-VCSH + ASI-V sampler, Shimadzu, Japan). As mentioned in Section S1 in the supplementary information, TOC analyses were conducted directly on unfiltered samples (raw), while DOC determinations were conducted after filtration at 0.45 µm. The particulate organic carbon was determined by subtracting TOC and DOC. Before usage, syringes (Terumo, Japan) and nylon filters (VWR, 0.45 µm, USA) were rinsed three times with ultrapure water and used to collect

samples during the first campaign at the PA swimming pool (PA1). For the remaining PA and PB samples, a glass filtration kit (cf. 2.3) was utilized. Additionally, the carbon (DOC and TOC) and total nitrogen concentrations were measured using another TOC-meter (Multi N/C 2100, Analytic Jena, Germany) for particle chlorination studies. The organic nitrogen content of FBW and filling water was determined using the Kjeldahl method after the ammonium concentration was subtracted, in accordance with ISO 5663 (1984). Nitrate concentrations (LOD: 0.5 mg L⁻¹) were determined utilizing the hydrazine reduction method (NF ISO 15923-1, 2014), nitrite concentrations (LOD: 0.010 mg L⁻¹) were determined utilizing the sulphanilamide method (NF ISO 15923-1, 2014), and ammonium concentrations (LOD: 0.050 mg L⁻¹) were determined utilizing the indophenol blue spectrophotometric method (NF T 90-015-2, 2000).

The particulate concentration was determined using the same glass filtration kit as for DOC measurement as well as the same filters and preparation method as during chlorination studies. The sample (200 mL) was filtered, and the filters were then dried in an oven for at least 4 h and weighed after cooling in ambient air.

The same device was used to determine free chlorine during particle chlorination tests as was used for on-site measurements of free and total chlorine. Fourteen DBPs, including four THMs, three HANs, five HAAs, CH, and TCP, were analysed. An aliquot (50 mL) of the sample was treated with 5 mL of MTBE and subsequently tested for these compounds. Sodium sulfate (10 g) was added, and the vials were vigorously shaken by hand for 2 min. Subsequently, the organic phases were recovered and added to chromatography vials for GC-ECD analysis (Perkin Elmer Clarus 580 system, PerkinElmer, Norwalk, CT, USA). HAAs were analysed as their methyl esters obtained after esterification with 10% H₂SO₄ methanolic solution and heating at 50°C for 2 hours. Table 1 provides details on the analysed compounds, their limits of detection (LOD), and their limits of quantification (LOQ).

Table 1: Analytical performances for the measurement of THMs, HANs, CH, and TCP by GC-ECD

	THMs				CH	HANs			TCP
	TCM	BDCM	DBCM	TBM		DCAN	BCAN	DBAN	
R ²	0.97	0.99	0.99	0.98	0.99	0.99	0.98	0.98	0.99
Range (µg/L)	0-100	0-20	0-20	0-50	0-50	0-20	0-20	0-20	0-20
Limits of detection	1.1	0.10	0.19	0.02	0.06	0.20	0.19	0.12	0.20
RSD	13%	5.9%	1.1%	2.7%	2.4%	2.6%	2.5%	2.3%	3.9%

The particles issued from PA FBW were also observed using a scanning electronic microscope (SEM, Zeiss EVO 15). 12 mL of FBW was previously filtered on a polyethersulfone filter (Grosseron, 0.1 µm, France), which was gently dried in an oven. The filter was then coated with a thin layer of gold before microscopic observations.

Particle-size distribution measurements (range: 0.017-2,000 µm) on FBW samples were conducted with a Malvern Master Sizer 3000. The refractive index was set at 0.18 for the red laser (632.8 nm) and 1.47 for the blue laser (470 nm), assuming that the particles were spherical. The refractive index of water for the red laser was set at 1.33. Dispersant (water) temperature was 20°C ± 2°C.

2.2 Particles chlorination protocol

Particles collected during PA4 were subjected to chlorination assays.

FBW (100 mL), either raw or diluted with ultrapure water (dilution factor of 2 or 8, based on experiments), were filtered using a glass filtration kit (Merck Millipore, USA) with fiberglass filters (Fisherbrand, 0.7 μm , USA). The resulting filtrates (filtered FBW) were analyzed for carbon and nitrogen content (see Section 3.5.1). The filters were then separated into two series. One was dried in an oven at 50°C for at least 4 h and weighed after cooling in ambient air to measure particle mass; the other was air-dried for the analysis of DBPs. These latter were then crushed with a mortar and a pestle. The filter fragments were then weighed and divided equally in mass (median value: 69.1-69.5 mg) into two series of three 66 mL glass tubes that had been heated to 500°C for 5 h and cooled to ambient temperature. One series of tubes was used for liquid-liquid extraction (LLE) of volatile DBPs (THMs, HANs, CH, and TCP) and the other one was used for LLE of HAAs, previously esterified with 10% H_2SO_4 methanolic solution, with minimal change to the EPA 551.1 and 552.2 extraction techniques (Manasfi et al., 2016). Without leaving any headspace, 3.3 mL of phosphate buffer (pH = 6.7, equivalent to the PA FBW value), diluted sodium hypochlorite solution, and ultrapure water were added to the glass tubes containing the filter fragments. The samples were then chlorinated at 1.2 $\text{mgCl}_2\text{L}^{-1}$ as free chlorine, which corresponds to the free chlorine concentration measured in PA FBW, and at 24 $\text{mgCl}_2\text{L}^{-1}$ as free chlorine maintain residual free chlorine after 5 d of reaction time (determined after previous experiments conducted on particles sampled during PA3; see Figure 2).

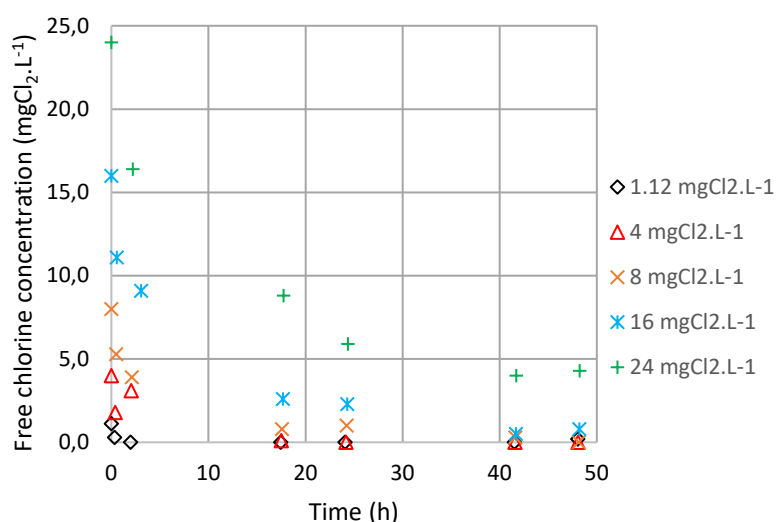


Figure 2. Remaining free chlorine ($\text{mgCl}_2\text{L}^{-1}$) during 48 hours experiments on particles collected during PA3 (particles concentration median value: 93 mg.L^{-1}). Free chlorine doses are given in the legend.

These two sets of three glass tubes were used for particle chlorination experiments and corresponded to the three reaction times of experiments (24 h, 48 h, and 96 h). Each sample represented one chlorine dose (1.2 or 24 $\text{mgCl}_2\text{L}^{-1}$ as free chlorine) and one concentration of particle matter (79.0 mgL^{-1} when initial free chlorine dose was 1.2 $\text{mgCl}_2\text{L}^{-1}$; 77.2 mgL^{-1} , 36.2 mgL^{-1} or 11.9 mgL^{-1} when initial free chlorine dose was 24 $\text{mgCl}_2\text{L}^{-1}$). Free chlorine was measured at each of the previously listed reaction times. The LLE-obtained organic extracts were finally analyzed using GC-ECD. The methodology for chlorination is summarized in Figure 3.

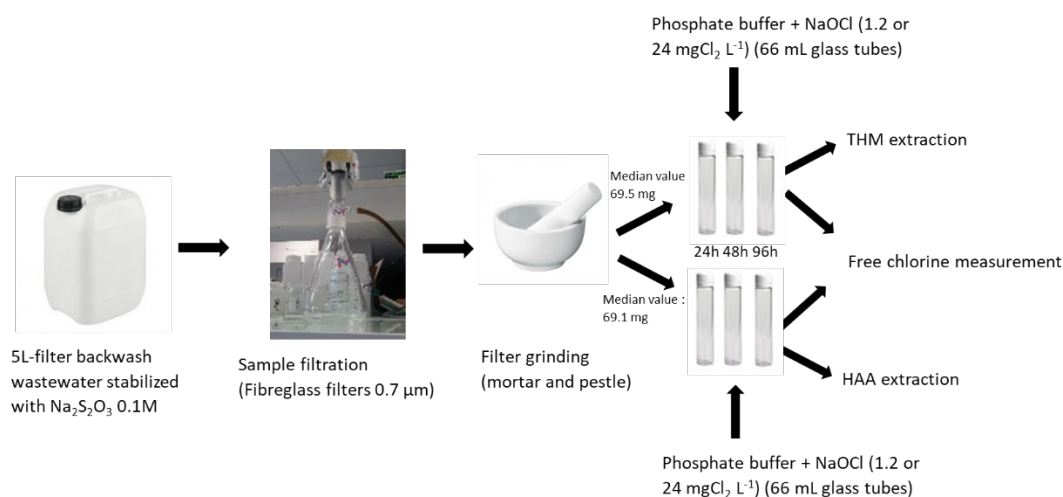


Figure 3. Diagram representing particles chlorination protocol

3. Results and discussions

3.1 Physico-chemical parameters measured in swimming pool samples

Similar pH ranges were observed in PA FBW and pool water (6.6-7.2 and 6.5-7.1, respectively) and in PB FBW (7.1 and 7.3, respectively). In PA, the pH of filling water ranged from 7.3 to 8.0, while in PB. It was determined to be 7.7 This discrepancy was the result of pH correction performed before water entered the pool. Conversely, conductivity values for filling water (411-499 $\mu\text{S}\cdot\text{cm}^{-1}$ in PA, 413 $\mu\text{S}\cdot\text{cm}^{-1}$ in PB) were lower than those for FBW (620-742 $\mu\text{S}\cdot\text{cm}^{-1}$ in PA and 562 $\mu\text{S}\cdot\text{cm}^{-1}$ in PB) and pool water (634-750 $\mu\text{S}\cdot\text{cm}^{-1}$ in PA and 560 $\mu\text{S}\cdot\text{cm}^{-1}$ in PB). This was caused by the ion-rich mineral salts released by bathers (mostly sweat) into the pool water, which was higher in ions than the filling water. The pH and conductivity readings results at both PA and PB are shown in the supplementary information (Figure 4).

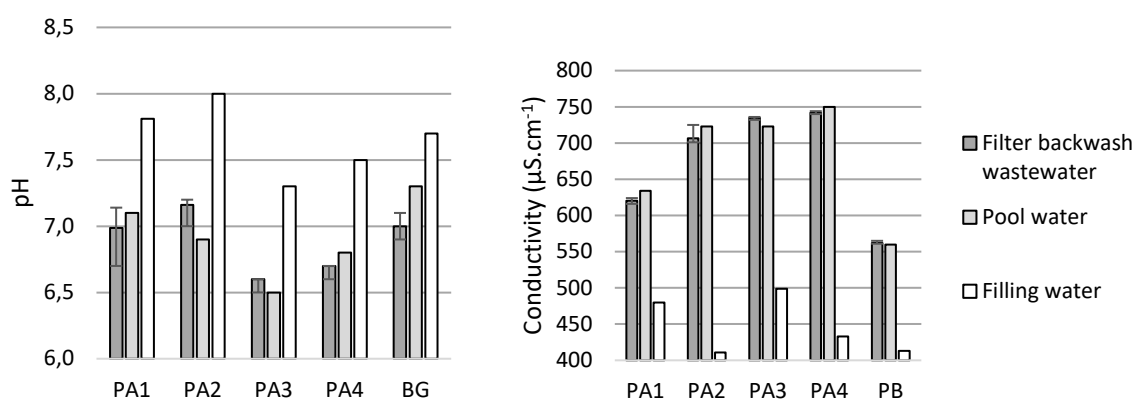


Figure 4. pH (a) and conductivity (b) measured in PA and PB during water sampling in filter backwash wastewater, pool water and filling water (drinking water). Backwash value correspond to mean of value of the 14 (PA1) and 5 (PA2) consecutive samples collected during the backwash process and 3 measures on samples PA3, PA4 and PB; errors bars correspond to min and max value observed during water sampling in filter backwash wastewater

Chlorine measurements performed on FBW, pool water, and filling water are shown in Figure 5. The free chlorine concentration in PA pool water (Figure 5a) was fixed between 1.4 and 1.6 $\text{mgCl}_2\text{L}^{-1}$, while PB pool water contained 1.5 $\text{mgCl}_2\text{L}^{-1}$. Free chlorine in FBW reached 0.9 to 1.5 $\text{mgCl}_2\text{L}^{-1}$ in PA and 1.6 $\text{mgCl}_2\text{L}^{-1}$ in PB. The total chlorine concentration (Figure 5b) in PA FBW ranged between 1.5 and 2.1 $\text{mgCl}_2\text{L}^{-1}$, whereas PB FBW contained 2.2 $\text{mgCl}_2\text{L}^{-1}$.

This indicates that the combined chlorine concentrations (total chlorine – free chlorine) in PA FBW were between 0.4 and 1.0 $\text{mgCl}_2\text{L}^{-1}$, while in PB FBW, they were 0.6 $\text{mgCl}_2\text{L}^{-1}$. Combined chlorine concentrations in the recreational pool water ranged between 0.2 and 0.4 $\text{mgCl}_2\text{L}^{-1}$ in PA and PB, respectively. Consequently, combined chlorine concentrations were higher in FBW than in pool water, indicating that particles may contribute to the formation of chloramines and of other inorganic chlorination by-products formation, as reported in the literature (Kim et al., 2002; Hansen et al., 2012). Nevertheless, according to data presented in Figure 10, the nitrogen level in water was almost four times higher (5.1 mgL^{-1}) than the nitrogen amount in particles (1.3 mgL^{-1}) and pool water (1.4 mgL^{-1}). At this step, combined chlorine concentration determinations could not be used to discriminate the role of particles in the formation of combined chlorine.

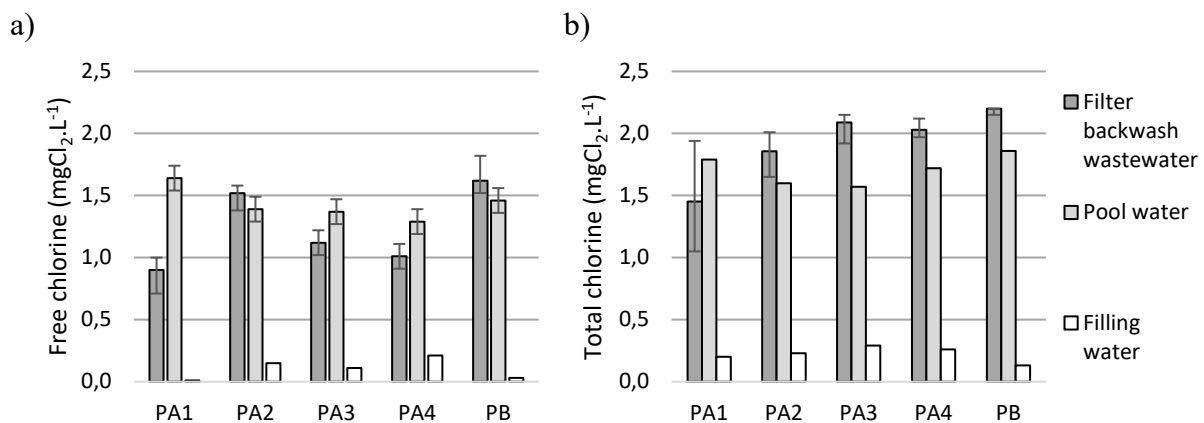


Figure 5. Free chlorine (a) and total chlorine (b) concentrations measured in PA and PB during water sampling in filter backwash waters, pool water and filling water (drinking water). Backwash values correspond to the average value of the 14 (PA1) and 5 (PA2) consecutive samples collected during the backwash process and to three measures on samples PA3, PA4 and PB; errors bars correspond to min. and max. values observed during water sampling for filter backwash water and to standard deviation ($0.1 \text{ mgCl}_2\text{L}^{-1}$) for free chlorine in pool water.

3.2 Turbidity and particles concentration and size distribution determination

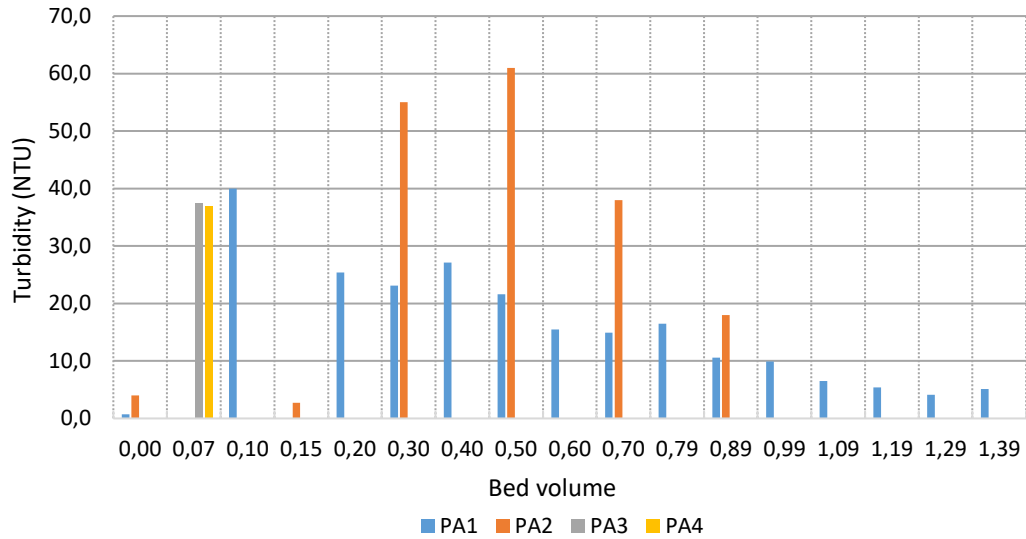
Initially, turbidity and particles concentrations in filling water were measured and found to be below the LOD for all monitoring periods.

The concentrations of turbidity and particles were plotted against BV (Figure 6) to compare samples obtained from different campaigns as the quantities of FBW corresponding to one sample could vary between sampling campaigns and across samples within the same campaign. During PA1, the turbidity maximum value was 40 NTU (Nephelometric Turbidity Unit) at a BV of 0.10, but the turbidity maximum value during PA2 was 61 NTU at a BV of 0.50 (Figure 6a). During PA1, the turbidity for comparable BV (0.30, 0.50, 0.70, and 0.89) was two to three times lower than during PA2. It could be explained by the fact that the time between backwashes was longer during PA2 (15 d) than PA1 (5). PA3 and PA4 exhibited comparable turbidity levels (around 37 NTU) with a BV of 0.07. Attendances in the recreational pool between PA3 and PA4 (80 and 221 bathers each day, respectively); however, these samples were collected when turbidity rose and after the same time interval between two backwashes (5 d).

During both PA1 and PA2, a maximum particle concentration of 90.0 and 91.1 mg L^{-1} was attained (Figure 6b) with a BV of 0.30. Contrary to the turbidity and with a BV of 0.70, the particle concentration during PA2 (36.0 mgL^{-1}) was lower than during PA1 (55.3 mgL^{-1}). When the BV was 0.89, the particles concentration during PA2 (20.3 mg L^{-1}) was twice as low as PA1 (39 mg L^{-1}). Figure 2b demonstrates that PA3 and PA4 had distinct particle concentrations (69.7 and 101.7 mg L^{-1}) at a BV of 0.07; however, their turbidities were comparable (37 NTU; Figure

6a). This demonstrates that turbidity and particle concentration levels are not absolutely associated, although turbidity remains the best operational measure of filtration efficacy for swimming pool managers. Thus, French rules have established a maximum turbidity level of 0.5 NTU for swimming pool water.

a)



b)

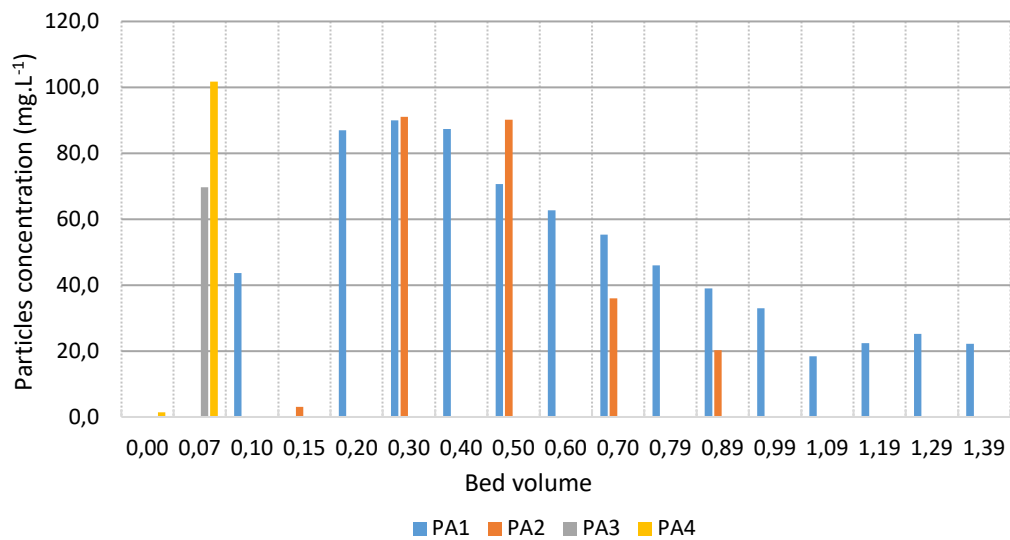


Figure 6. Turbidity (NTU; a) and particle concentration ($\text{mg}\cdot\text{L}^{-1}$, b) versus backwash bed volume. Values of turbidity and particle concentration for bed volume at 0.00 correspond to those measured in pool water for each campaign at PA.

The particle size distributions of samples obtained during the four campaigns were also determined. The volumetric percentage curves of particles sampled during the other campaigns (PA2, PA3 and PA4) exhibited two maximum values between 0.6 and 0.7 μm and 18 and 24 μm with the exception of PA1 samples (where only one maximum value was observed) (Figure 7).

a)

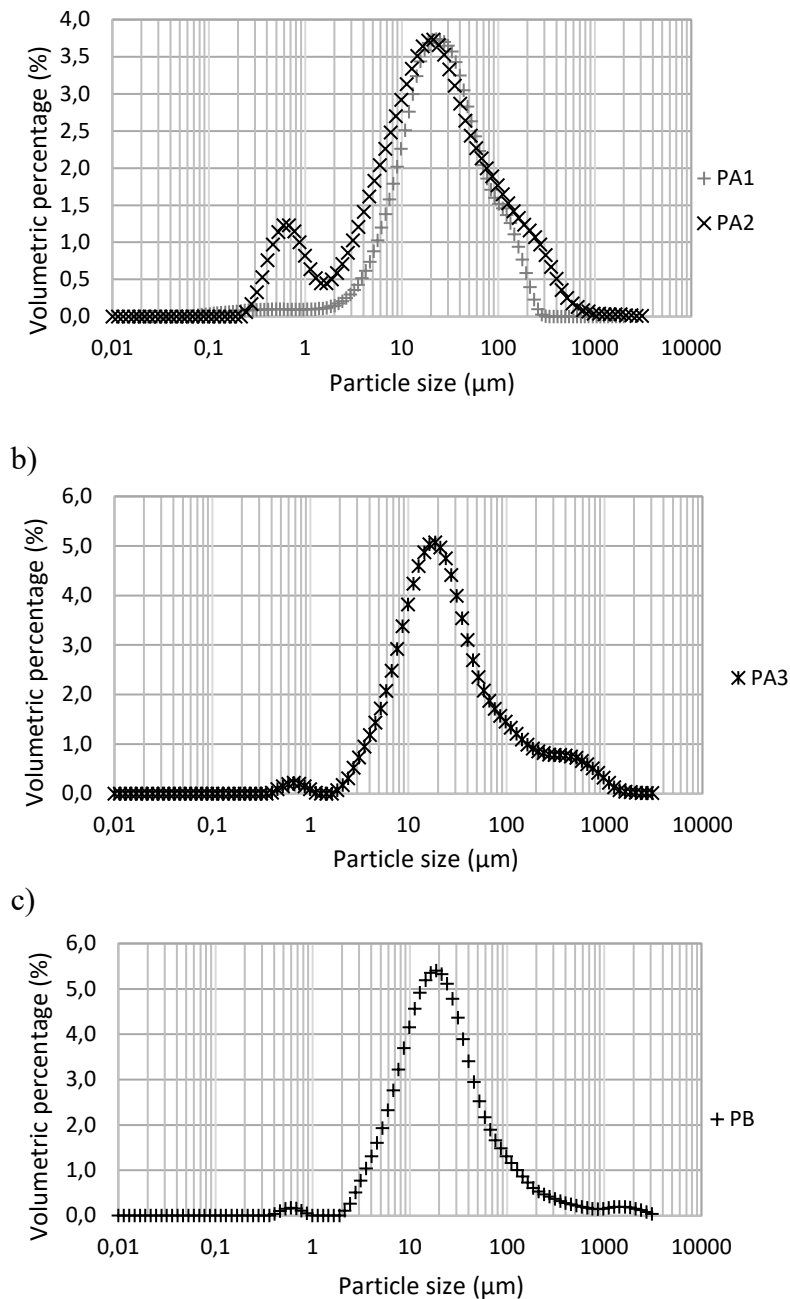


Figure 7. Particle size distribution curves of filter backwash wastewater samples issued from PA and PB swimming pools

Between 100 and 300 μm, a knee-point was also seen for the entire dataset. Based on the relation between the efficiency of various filter media and mode of filtration and the size of molecules and particles found in swimming pools (Figure 8, ANSES, 2020), the first maximum value recorded for submicron particles may correspond to bacteria. The second maximum value across all campaigns may correspond to retained human material near the top of the media. The knee-points seen between 100 and 300 μm could be explained to the presence of media in the samples as particles of flint have the same size.

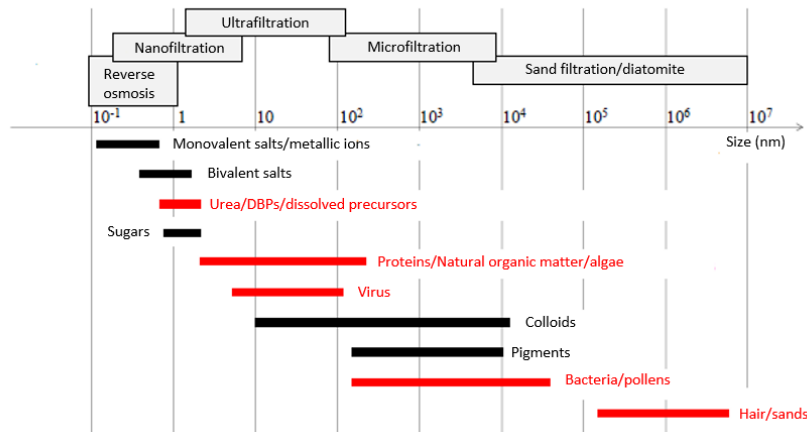
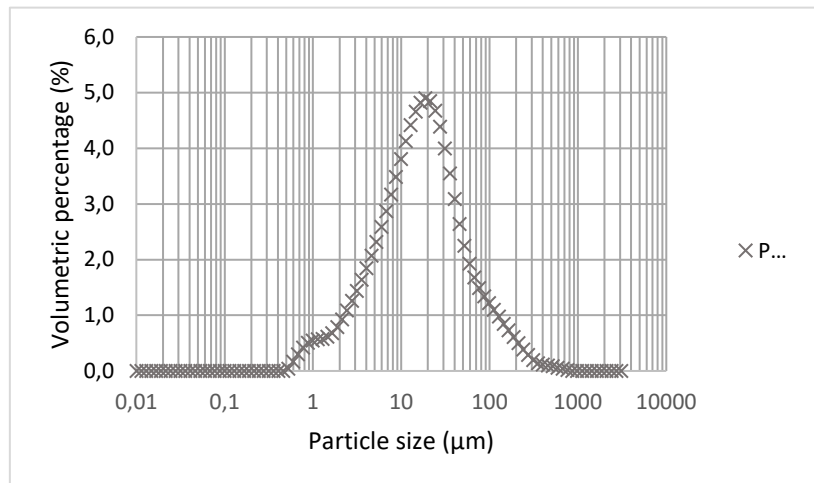


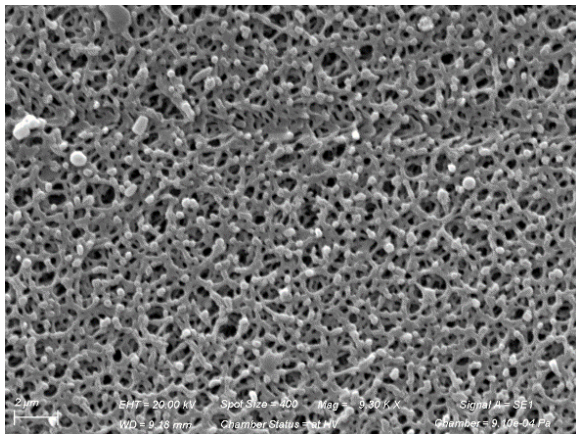
Figure 8. Efficiency of different filter media and mode of filtration versus the size of molecules and particles found in swimming pools (translated from ANSES, 2020)

To better describe the collected particles, microscopic observations were performed on a PA4 sample. Figure 9 depicts the particle-size distribution and SEM measurements performed on that sample. Figure 9a shows two maximum values as previously observed during the other campaigns, with a small shift for the little maximum in terms of particle size (1 μm) compared to other analysed samples. A second maximum value was observable, as previously seen, for particle size of around 19 μm (volumetric percentage: 4.9 %). Figure 9c shows the presence of aggregates on the filter, probably corresponding to a mixture of anthropogenic material and coagulant used before filtration step. Some spherical clusters were also observable above some previous aggregates. One of these spheres had a measured diameter between 0.6 and 0.7 μm , corresponding to similar particle size than observed in almost all particle size curves. These observations may suggest that there were bacteria in this sample (as suggested by their particle size and comparison with Figure 8). However, it was not possible to confirm their presence by the SEM observation. Some additional tests will be required to identify the presence of bacteria in this sample and determine which type of bacteria could be found.

a)



b)



c)

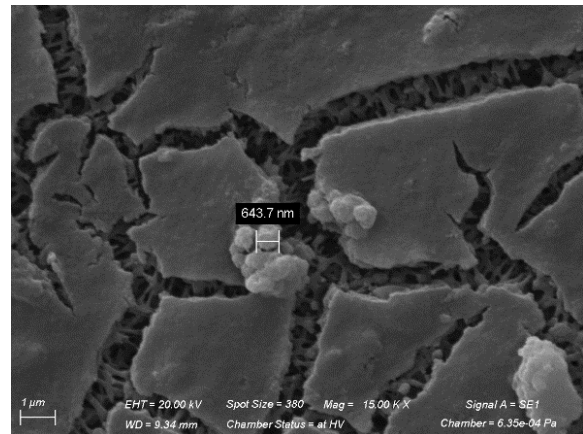


Figure 9. Particle size determination in PA4 sample (a), filter structure for particles recovery (b) and particles from filter backwash water observation in PA4 sample (c)

3.3 Carbon and nitrogen analyses

3.3.1 Determination of carbon and nitrogen concentration in particulate matter

Carbon and nitrogen concentrations were measured in FBW and filtrated-FBW (FBW filtered at 0.7 μm , as described in Section 2.3). Analyses were conducted on samples taken during PA4 (BV of 0.14), as this sampling campaign corresponded to the highest attendance (221 bathers per day) and was expected to permit the sampling of a higher particle concentration.

Figure 10a demonstrates that the content of organic carbon in FBW was 19.6 mgCL^{-1} as compared to 3.3 mgCL^{-1} in filtrated FBW. The total nitrogen concentration (Figure 10b) in FBW and filtrated FBW reached 5.1 mgNL^{-1} and 3.8 mgNL^{-1} , respectively. The difference in concentration between FBW and filtrated FBW yields a carbon concentration of 16.3 mgCL^{-1} in the particle phase. Similarly, the concentration of nitrogen in the particle phase was 1.3 mgNL^{-1} . In accordance with the BFA formulation from Judd and Bullock (2003), filtrated FBW included more nitrogen than carbon. However, the nitrogen to carbon ratio from these results (1.1 mgN.mgC^{-1}) was different from BFA's ratio (1.6 mgN.mgC^{-1}). Seux (1988) demonstrated

that the dissolved pollution brought by bathers was between 0.55 and $1 \text{ g TOC.bather}^{-1}.\text{h}^{-1}$ and between 0.8 and $0.9 \text{ KN.bather}^{-1}.\text{h}^{-1}$, resulting in an N/C ratio between 0.9 and 1.6 (mgN.mgC^{-1}).

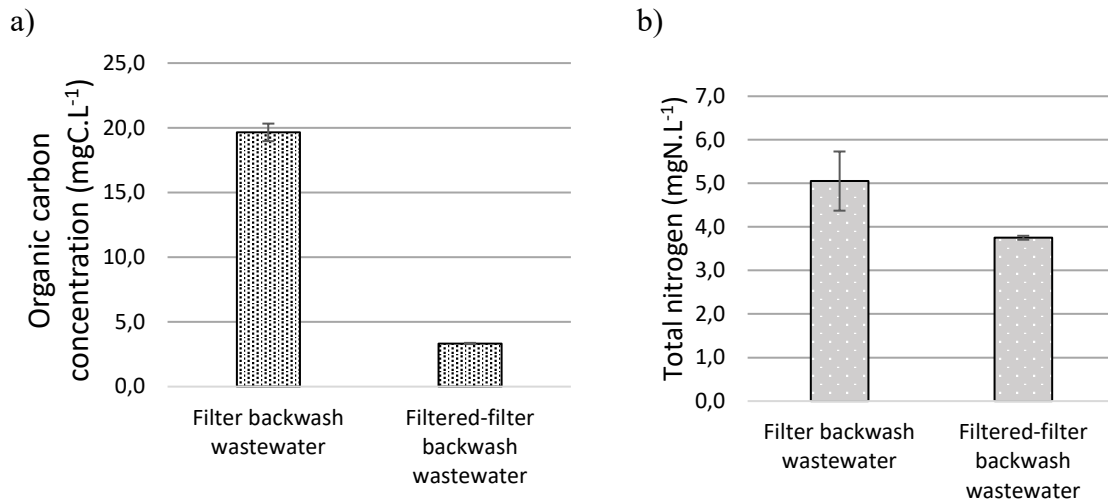


Figure 10. Organic carbon (a) and total nitrogen (b) content in PA filter backwash wastewater

Concerning the nitrogen and carbon content of particles, our research indicates that the carbon concentration is four times greater than the nitrogen concentration, with an N/C ratio of 0.25. These results are in accordance with the findings of Keuten (2014), who examined the sum of particulate and dissolved pollutants released by bathers during controlled sweat tests ($500 \text{ mgC.bather}^{-1}.\text{h}^{-1}$ and $154.6 \text{ mgN.bather}^{-1}.\text{h}^{-1}$, equating to an N/C ratio of 0.3).

3.3.2 Carbon and nitrogen releases in indoor swimming pools

Following measured concentrations during PA1 and PA2 (shown in Figure 11) and the projected FBW volume used to determine BV, carbon and nitrogen releases were calculated. To calculate particulate carbon, DOC was subtracted from TOC. As FBW sampling was conducted on one of the three filters, the FBW flow was determined to be $83.3 \text{ m}^3.\text{h}^{-1}$, which corresponds to a third of the recirculation flow at PA. It was expected that there were 80 bathers per day during PA1 and 75 bathers per day during PA2 (only schoolchildren were present) and that around 80% of the bathers used the recreational pool. Time spent by bathers in the recreational pool was considered to be 1 h, a duration usually employed when conducting risk assessments (ANSES, 2012).

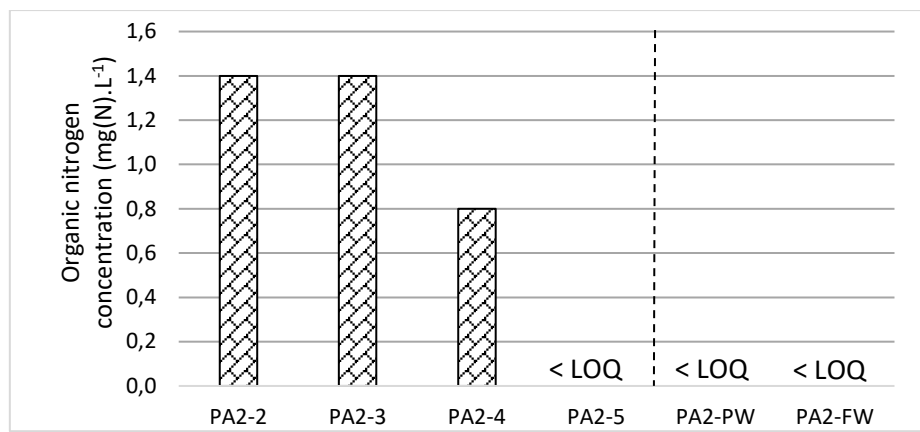
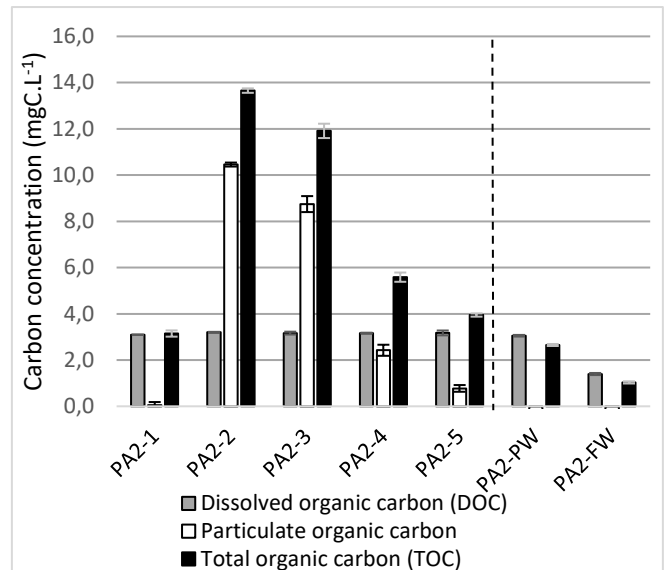
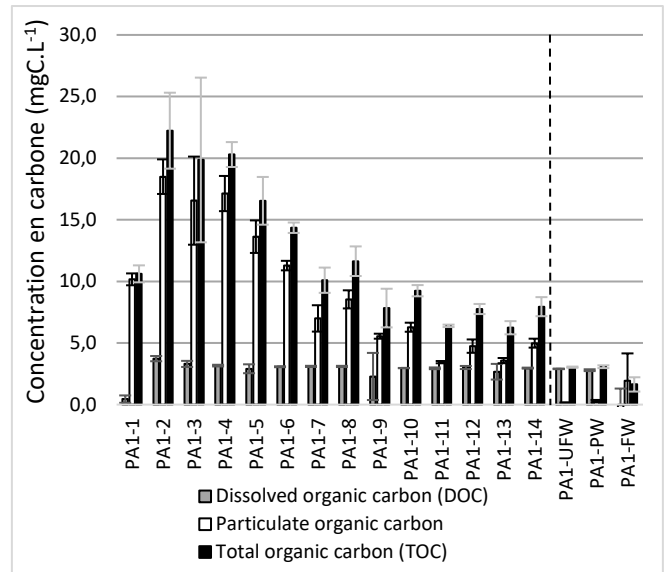


Figure 11. FBW carbon content sampled during PA1 (a) and during PA2 (b) and FBW organic nitrogen content during PA2 (c). Numbers (1 to 15) affiliated with the campaigns (PA1 or PA2) are given in the order of sampling. (UFW: Ultrafiltered water; PW: Pool water; FW: Filling water).

TOC release was predicted to be around 80g of carbon for 5 d during PA1 (Table 1) and slightly more than 31 g for 15 d during PA2 in the swimming pool. This translates to 198.0 and 28.2 mgC.bather⁻¹.h⁻¹ TOC releases, respectively. Particulate carbon (TOC-DOC) appeared to represent the majority of carbon across both campaigns, with concentrations of 152.1 mg C bather⁻¹ h⁻¹ during PA1 and 16.4 mgCbather⁻¹ h⁻¹ during PA2, respectively. The estimated amount of nitrogen released during PA2 was 5.4 mgN.bather⁻¹.h⁻¹. Keuten et al. (2014) estimated that NPOC release reached an average of 500 mgC.bather⁻¹.h⁻¹, with a range between 60 and 1006 mg C bather⁻¹ h⁻¹ depending on the physical activities and pool temperature. The calculated total nitrogen release was 154.6 mgN.bather⁻¹.h⁻¹, with a range of 88 to 322 mgN.bather⁻¹.h⁻¹. Multiple factors, such as pool temperature, type and duration of activities (swimming and aquagym), daily attendance, and individual differences contribute to these substantial variances in release rates (Keuten et al., 2014; Parinet et al., 2012).

Table 1. Estimated carbon and nitrogen releases in PA (n.d.: not determined).

Campaign	PA4	PA2
Number of days since the last filter backwashing	5	15
Sampling date	22/09/2020	11/06/2021
TOC released (mgC)	79181.6	31525.9
Hourly TOC released per bather (mgC.bather ⁻¹ .h ⁻¹)	198.0	28.2
DOC released (mgC)	18360.7	13167.8
Hourly DOC released per bather (mgC.bather ⁻¹ .h ⁻¹)	45.9	11.7
Particulate organic carbon released (mgC)	60820.9	18358.1
Hourly particulate organic carbon released per bather (mgC.bather ⁻¹ .h ⁻¹)	152.1	16.4
Organic nitrogen released (mgN)	n.d.	6018.3
Hourly organic nitrogen released (mgN.bather ⁻¹ .h ⁻¹)	n.d.	5.4

3.4 Particles chlorination

To examine the production potential of various DBPs from particles released by bathers, particles were chlorinated. PA4 involved the collection of particles. Two free chlorine doses (1.2 and 24 mgCl₂.L⁻¹) and particle concentrations (79.0 mgL⁻¹ for chlorine dose at 1.2 mgCl₂.L⁻¹ -experiment 1-, 77.2 -experiment 2-, 36.2 -experiment 3- and 11.9 mgL⁻¹ -experiment 4- for chlorine dose at 24 mgCl₂.L⁻¹) were tested during experiments conducted in duplicate and according to the protocol presented in Section 2.3. In preliminary blank experiments, the potential chlorine consumption of raw filters for a free chlorine dose of 24 mgCl₂.L⁻¹ measured at 26.5% within 48h has been evaluated (Figure 12).

Initial free chlorine dose (mgCl ₂ L ⁻¹) ¹⁾	24		
Particle concentration (mg L ⁻¹)	0		
Time (h)	24	48	96
Consumed chlorine (%)	17.5	26.5	25.0
DBP	Concentrations (µg.L ⁻¹)		
TCM	6.6	100.0	26.6
BDCM	<LOQ	0.6	0.9
DBCM	0.3	0.3	0.3
DCAN	<LOQ	<LOQ	<LOQ
CH	1.3	5.8	28.2
TCP	<LOQ	<LOQ	<LOQ
MCAA	<LOQ	<LOQ	<LOQ
DCAA	<LOQ	<LOQ	5.1
TCAA	5.0	6.2	14.1
BCAA	<LOQ	<LOQ	<LOQ
BDCAA	<LOQ	<LOQ	<LOQ

Figure 12. Free chlorine consumption and DBPs formation from raw filter (blank experiments)

3.4.1. Kinetics of free chlorine consumption

Table 2A displays the measurements of free chlorine at three-time intervals (24 h, 48 h, and 96 h) as a function of the initial dose of free chlorine and initial particle concentration. At a low amount of free chlorine (1.2 mgCl₂L⁻¹) and a high concentration of particles (79 mgL⁻¹), free chlorine was rapidly consumed (within the first 24 hours). Increasing the initial amount of chlorine (24 mgCl₂L⁻¹) for roughly the same level of particles (77.2 mgL⁻¹) afforded a sluggish and moderate consumption of free chlorine (around 20% within 24 h and around 40% within 96 h). Reducing the level of initial particles (experiments 2, 3, and 4) had little effect on chlorine consumption when initially applied at a high dose (24 mg Cl₂L⁻¹), even though a higher consumption within 96 h was observed for the highest dose of particle tested (40% during experiment 2 versus 17% in experiments 3 and 4).

These results reveal that particles are capable of reacting with chlorine and may be regarded as precursors to DBPs along with other dissolved compounds. During these chlorination trials, DBPs were monitored, and analytical data are shown below.

3.4.2 DBPs formed during particles chlorination assays

As DBPs may have been present prior to chlorination experiments (as particle samples are actual samples collected from FBW), the results presented in Table 2B reflect the levels of DBPs actually formed during chlorination experiments (DBPs = DBPs formed during chlorination – initial DBPs concentration). In addition, as DBPs might be formed by the reaction of free chlorine with the fiberglass filter used to collect particles, parallel studies with untreated fiberglass filters were done to solely evaluate DBPs formed during particle chlorination assays. Within 96 h of chlorination of raw fiberglass filters (Figure S9) at 24 mgCl₂.L⁻¹, substantial amounts of TCM (26.6 µgL⁻¹), CH (28.2 µgL⁻¹) and TCAA (14.1 µgL⁻¹) were formed. Other DBPs such as BDCM (0.9 µgL⁻¹), DBCM (0.3 µgL⁻¹), and DCAA (5.1 µgL⁻¹) were also produced in low amounts within 96 h. These findings demonstrate that chlorine consumption of raw filters cannot be explained solely by chlorine absorption but also by chemical interactions between fiberglass filter and chlorine.

Table 2. Free chlorine consumption (2A) and DBP formation (2B) within 24, 48 and 96 hours depending on initial free chlorine concentration and particles concentration

# Experiment		Experiment 1			Experiment 2			Experiment 3			Experiment 4		
3A	Time (h)	24	48	96	24	48	96	24	48	96	24	48	96
	Initial free chlorine concentration (mgCl ₂ .L ⁻¹)	1.2			24			24			24		
	Remaining free chlorine concentration (mgCl ₂ .L ⁻¹)	0.1	0	0.08	21.6	19.6	14.4	22.5	19.7	19.7	22.1	22.7	20.0
	Particles concentration (mg.L ⁻¹)	79.0			77.2			36.2			11.9		
DBP		Concentrations (µg.L⁻¹)											
3B	TCM	18.5	17.2	25.7	43.1	52.1	201.4	36.0	87.0	90.5	8.3	36.6	67.0
	BDCM	1.3	0.9	1.2	2.5	2.4	3.7	1.3	1.6	2.4	0.6	0.8	1.2
	DBCM	0.2	0.2	0.2	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
	DCAN	2.9	3.0	3.6	9.8	14.2	10.9	5.1	10.7	5.8	1.4	3.3	1.5
	CH	1.3	3.0	5.1	9.7	17.8	46.0	5.6	17.4	18.7	2.1	8.7	11.9
	TCP	<LOQ	<LOQ	<LOQ	1.4	1.6	2.3	0.8	1.6	1.6	<LOQ	0.9	0.9
	MCAA	<LOQ	<LOQ	<LOQ	<LOQ	7.2	14.1	<LOQ	5.5	6.6	<LOQ	<LOQ	<LOQ
	DCAA	4.0	6.8	6.1	24.8	59.6	129.8	14.9	43.6	87.9	3.6	20.4	40.5
	TCAA	3.2	9.6	12.0	42.5	90.9	231.8	27.6	64.0	126.2	11.0	33.4	56.2
	BCAA	<LOQ	<LOQ	<LOQ	<LOQ	0.5	1.2	<LOQ	<LOQ	0.7	<LOQ	<LOQ	<LOQ
	BDCAA	<LOQ	<LOQ	<LOQ	<LOQ	3.0	5.7	<LOQ	2.6	<LOQ	<LOQ	<LOQ	<LOQ

Within 96 h, TCM concentrations reached a maximum of 25.7 µg.L⁻¹ when a high amount of particles was chlorinated with a modest initial dosage of free chlorine (experiment 1). Increasing the initial dose of chlorine to the same amount of particles (experiment 2) led to the formation of a greater variety of DBPs, with TCAA (231.8 µg.L⁻¹ within 96 h) being the highest, followed by TCM (201.4 µg.L⁻¹) and DCAA (129.8 µg.L⁻¹). The similar dominance of these three DBPs was also found in experiments 3 and 4, with the greatest concentrations corresponding to the highest particle concentrations. For example, TCAA levels reached a maximum of 231.8 µg.L⁻¹, 126.2 µg.L⁻¹, and 56.2 µg.L⁻¹, respectively, at starting particle concentration of 77.2 mg.L⁻¹, 36.2 mg.L⁻¹, and 11.9 mg.L⁻¹. The similar tendency was observed for the other DBPs under investigation: levels of BDCM, DBCM, DCAN, CH, TCP, MCAA, DCAA, BCAA, and BDCAA were proportional to initial particle concentrations.

Higher concentrations of HAAs relative to THMs may be explained by the greater stability of HAAs in water, even in the presence of high residual chlorine concentrations (Kanan and Karanfil, 2011). Hansen et al. (2012) discovered a higher formation of HAAs (9.6 µmolmgDOC⁻¹) when particles were chlorinated with 35 mgCl₂.L⁻¹ of free chlorine, followed by THMs (4.0 µmolmgDOC⁻¹) and HANs (1.6 µmolmgDOC⁻¹) after 48 h of reaction time. In accordance with the results of chlorination at 24 mgCl₂.L⁻¹ and particle concentration at 77.2 mg.L⁻¹ after 48 h of reaction time, the order of DBPs families was determined. The relative formation of HAAs (0.31 µmolmgDOC⁻¹) was the highest, followed by THMs (0.13 µmolmgDOC⁻¹) and HANs (0.04 µmolmgDOC⁻¹). These results were lower than those found by Hansen et al. (2012). However, DOC values were not identical (3.3 mgCL⁻¹ during our experiments against 125 µg.L⁻¹ during Hansen's experiments conducted with > 10 µm particles released from a hot tub with a 6-min filter flush). Despite discrepancies between the two trials, the ratios of HAAs/THMs and HANs/THMs were comparable, at 2.4 (2.3 during Hansen's experiments) and 0.4 (0.3 during Hansen's experiments), respectively. Table 3 also verifies that relative DBPs formation resulting from chlorination of FBW equals the sum of DBPs formed by chlorination of filtrated FBW and particles.

Table 3. Relative DBPs formation within 48 hours from chlorination at 24 mgCl₂.L⁻¹ i) of filter backwash wastewater (FBW), ii) of filtered-filter backwash wastewater (filtered-FBW) and iii) of particles at a concentration of 77.2 mg.L⁻¹ (DOC: 3.3 mgC.L⁻¹). Results from chloroform (molar mass: 119.38 gmol⁻¹) were used for THM, from DCAA and TCAA (128.94 and 163.38 gmol⁻¹ respectively) for HAAs and from DCAN (109.94 g mol⁻¹) for HAN

	THM	HAA	HAN	HAA/THM	HAN/THM
	($\mu\text{mol mg DOC}^{-1}$)	($\mu\text{mol mg DOC}^{-1}$)	($\mu\text{mol mg DOC}^{-1}$)		
Filter backwash wastewater (FBW)	0.26	0.69	0.09	2.7	0.4
Filtered-filter backwash wastewater (Filtered-FBW)	0.10	0.37	0.02	3.6	0.2
Particles	0.13	0.31	0.04	2.3	0.3

Except within 48 h, when DCAA concentration was 59.6 $\mu\text{g L}^{-1}$ and TCAA concentration was 90.9 $\mu\text{g L}^{-1}$, DCAA concentration was approximately double that of TCAA.

CH, which is regarded as possibly carcinogenic (Salmon et al., 1995), had lower concentrations than TCAA and TCM but reached substantial levels (up to 46.0 $\mu\text{g L}^{-1}$) within 96 h with a chlorine dose of 24 mgCl₂.L⁻¹ and a particle concentration of 77.2 mg L⁻¹.

DCAN concentrations were lower than those of TCM and TCAA, which might be explained by the lowest nitrogen concentration in particles, at 1.3 mgNL⁻¹, as shown in Figure 10b, compared to carbon concentrations (16.3 mgL⁻¹; Figure 10a).

4. Conclusions

Even at low concentrations, the particles released by bathers (mostly comprising hair and skin cells) contribute to the formation of DBPs when exposed to chlorine. In fact, a chlorine concentration of 1.2 mgL⁻¹ led to the formation of many DBPs, with TCM being the most abundant (25.7 $\mu\text{g L}^{-1}$ for TCM within 96 h).

It has been discovered that approximately half of the DBPs produced during the chlorination of FBW are derived from particles introduced by bathers.

These results question the frequency of filter cleaning as maintained by pool operators, particularly when sand filtration is utilized (with or without coagulation). For example, the French laws require the backwashing to begin when the water flow rate at the filter media outlet falls below 70% of the original flow rate (obtained when filter media is new). In the two pools studied, the filter cleaning was started up between two and four times per month. These long backflush cycles result in long contact durations between particles deposited in the filter bed and chlorine, which contributes to the formation of DBPs.

The formulation of BFA, which is intended to symbolize the pollution carried by bathers, is also a source of worry. As particles are the source of approximately 50% of DBPs, it may be of relevance to include this percentage to more accurately represent the anthropogenic pollutants released in swimming pools.

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